

**Final Report, Army Research Office**

**Principal Investigator:** Fredric M. Menger

**Title:** *New Colloidal Systems with Practical Ramifications*

**Research Agreement No.:** DAAD19-01-0551

**Dates of Report:** May 30, 2001 –May 31, 2004

**Funds Remaining on May 31, 2004:** None      **Patents:** None

**Publications Acknowledging ARO Support in the Grant Period:**

- 1) F. M. Menger and A. L. Galloway, to be published in *J. Am. Chem. Soc.* "Contiguous vs. Segmented Hydrophobicity in Micellar Systems."
- 2) F. M. Menger, A. L. Galloway, M. E. Chlebowsky, and R. P. Apkarian *J. Am. Chem. Soc.* **2004**, 126, 5987. "Ultrastructure in Frozen/Etched Saline Solutions: On the Internal Cleansing of Ice."
- 3) F. M. Menger, A. L. Galloway, and D. G. Musaev *Chem. Commun.* **2003**, 2370. "Relationship between Rate and Distance."
- 4) F. M. Menger *Proc. Natl. Acad. Sci. U.S.* **2002**, 99, 4818. "Supramolecular Chemistry and Self-assembly."
- 5) F. M. Menger and V. A. Azov *J. Am. Chem. Soc.* **2002**, 124, 11159. "Synthesis and Properties fo Water-Soluble Asterisk Molecules."
- 6) F. M. Menger, H. Zhang, K. L. Caran, V. A. Seredyuk, and R. P. Apkarian *J. Am. Chem. Soc.* **2002**, 124, 1140. "Gemini-Induced Columnar Jointing in Vitreous Ice. Cryo-HRSEM as a Tool for Discovering New Colloidal Morphologies."
- 7) V. A. Migulin and F. M. Menger *Langmuir* **2001**, 17, 1324. "Adamantane-Based Crystals with Rhythmic Morphologies."

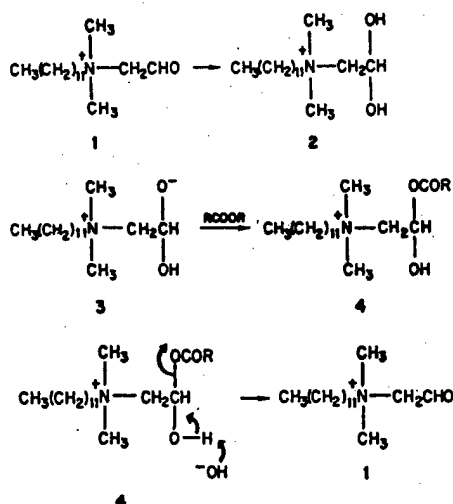
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## Report

May 31, 2004 marks the end of a 2-decade long association between my research group and the ARO. From my point of view, and I hope from the ARO's also, it has been a productive relationship. Above all, I appreciate how Drs. Ghiardelli, Seiders, and Lee have given me the freedom to let our imaginations wander and thus to produce the best chemistry we are capable of pursuing. In a spirit of nostalgia, I would like to summarize below some of the highlights of our ARO-funded research, particularly those papers directly related to decon of CWA.

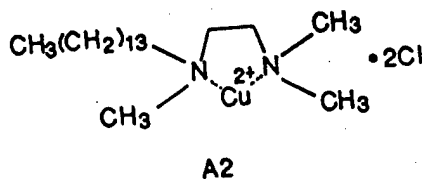
- 1) F. M. Menger and L. G. Whitesell, *J. Am. Chem. Soc.* **1985**, *107*, 707. "A Protease Mimic with Turnover Capabilities."

This paper described the synthesis of a micellar aldehyde (dubbed "Atlanta 1") whose hydrate would attack and hydrolyze bound esters. The important point is that the ester cleavage occurred with *turnover*, i.e. with a true enzyme-like catalysis which, at that time, was a rather unique mechanism.



- 2) F. M. Menger, L. H. Gan, E. Johnson, and D. H. Durst *J. Am. Chem. Soc.* **1987**, *109*, 2800. "Phosphate Ester Hydrolysis Catalyzed by Metallomicelles."

A metallomicelle containing copper (dubbed "Atlanta 2") was found to hydrolyze phosphate esters with rate accelerations approaching  $10^5$ . The combination of micellar binding and metal catalysis led to a remarkable catalysis for nerve agent simulants.



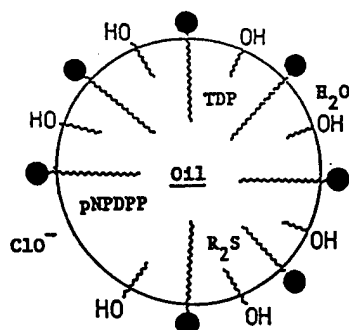
- 3) F. M. Menger and A. R. Elrington *J. Am. Chem. Soc.* **1990**, *112*, 8201. "Rapid Deactivation via Microemulsion Technology."

F. M. Menger and A. R. Elrington *L'Actualite chimique* **1991**, 177. "Formulating Microemulsions that Decontaminate a Toxic Substance."

F. M. Menger and H. Park *Recl. Trav. Chim. Pays-Bas Journal* **1994**, *113*, 176. "Microemulsions as Reaction Media. Self-organizing Assemblies in an Environmental Cleanup Problem."

F. M. Menger and M. J. Rourke *Langmuir*, **1999**, *15*, 309. "Deactivation of Mustard and Nerve Agent Models via Low-Temperature Microemulsions."

Prior to the 1990's, the emphasis had been on micellar catalysis, but it became evident that micelles have a major disadvantage: their solubilization capacity is low. It was for this reason that we switched to oil-in-water microemulsion systems that had a much greater ability to solubilize water-insoluble organics such as mustard. Probably our most important achievement in this area was a complex system that contained 11 components: propylene glycol, oil, stabilizer, two nerve agent simulants, and a mustard simulant. Reactions at 25° took place in seconds or over many minutes. Only by virtue of self-assembly does this extraordinarily complex mixture adopt a useful molecular organization. Since the microemulsion has the important property of resisting freezing, it does not have to be kept warm in a cold climate. Note that our microemulsion has similarities to DeconGreen, developed recently at Aberdeen. It too uses propylene glycol as a major component of the solvent system. In contrast to our household bleach being the reactant, DeconGreen uses fairly concentrated hydrogen peroxide (35%). Hydrogen peroxide is less reactive than hypochlorite, thereby requiring the presence of a metal catalyst. Both our low-temperature microemulsion and the DeconGreen must be prepared prior to use (in our case at least a week), thus skirting the desirability (and in my view impossibility) of having a non-caustic single-solution with a shelf-life of 5 years.



**Figure 1.** The 8-component oil-in-water microemulsion used in this study. NPDPP, TDP, and  $R_2S$  are three contaminants in the oil droplet (see text) which are destroyed by hypochlorite in the aqueous phase. Surfactant (heavy dots with tails) and cosurfactant (alcohol) stabilize the oil droplet.

- 4) The preceding lists papers directly relate to the decon problem. But there were many other ARO-supported publications that delved into related subjects such as the mechanistic source of fast catalytic rates; the construction of new catalytic polymers (i.e. high-porosity, copper-containing polymers); packing behavior in monomolecular films; ion conductance in lipid monolayers; giant vesicles; transport through liquid membranes; synthesis of organic self-assembled fibers; synthesis of new polyhydroxylated surfactants; enzyme-vesicle interactions for detection and release; remote steric effects; and synthesis of asterisk molecules.

ARO-supported papers in these areas have been listed in previous reports and will not be repeated here. The point here is that ARO funding over the years has been critical to the diversity and richness of our research program area, and both my students and I greatly appreciate this assistance.

## Report Summary of Current Grant

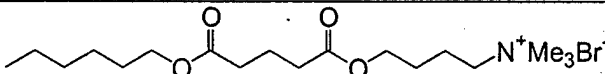
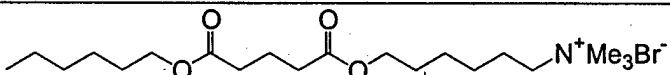
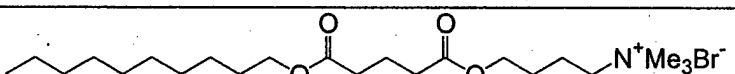
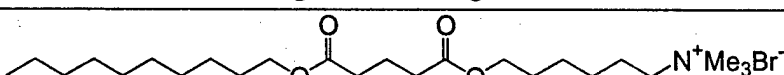
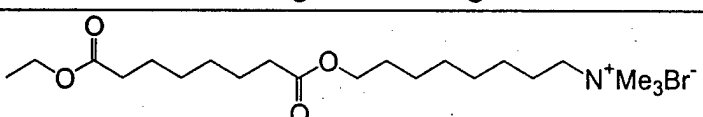
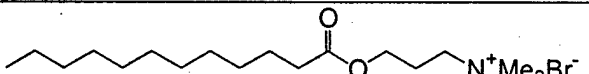
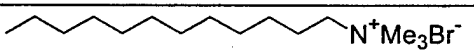
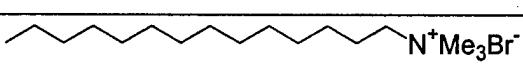
### 1) Ester-Modified Surfactants

On the next page are listed six new ester-containing cationic surfactants and a few of their colloidal properties. The project had two purposes: (a) We wanted to determine if endowing surfactant chains with ester groups could improve the solubilizing capacity of their micelles (much as ethyl acetate is a better solvent than hexane). (b) We wanted to compare the hydrophobicity of a contiguous hydrocarbon chain (e.g. a dodecyl chain) with that of an equivalent number of carbons but segmented (e.g. two ester-separated six-carbon chains).

We found that in three of the surfactants (**A**, **B**, and **E**) segmentation was deleterious to colloidal properties such as aggregation number and solubilization power. On the other hand, the three other surfactants (**C**, **D**, and **F**) were much more conventional in their colloidal properties. In fact, **D** solubilized mesitylene more effectively than did DTAB and TTAB (see Table). A long discussion of the surfactants will appear in a *J. Am. Chem. Soc.* paper that is now in press. Its Abstract summarizes are main findings:

This paper addressed a question not yet posed systematically in surfactant chemistry: How do the colloidal properties of surfactants respond to insertion of non-hydrocarbon functionalities (i.e. ester groups) within chains that are normally entirely hydrocarbon? In answering this question, two classes of such chain-modified surfactants were discovered. One class forms only small aggregates with non-cooperative self-assembly, low foaming, high areas of occupancy at the air/water interfaces, and weak solid adsorption and solubilization properties. The other class is much more normal with regard to their properties and, in fact, can even exceed conventional surfactants in mesitylene solubilization. Differences between the two

## Ester-Modified Surfactants

<i>Label</i>	<i># CH<sub>2</sub>'s</i>	<i>Structure</i>
A	12	
B	14	
C	16	
D	18	
E	15	
F	13	
DTAB	11	
TTAB	13	

<i>Surfactant</i>	<i>CMC, mM</i>	<i>Area, Å<sup>2</sup></i>	<i>Foam Vol., mL</i>	<i>TMS, mM</i>	<i>Mesitylene, mM</i>
A	2.4	81	0.01	0	1.7
B	2.5	123	0.48	0.026	5.3
C	2.2	75	2.5	1.2	38
D	1.4	75	3.2	5.2	93
E	1.0	334	0.04	0	0
F	4.6	54	3.5	5.4	27
DTAB	13.3	64	1.9	0.51	13
TTAB	3.3	52	3.3	7.9	36

categories of chain-modified surfactants originate from the degree of segmentation of the hydrocarbon and, in particular, upon the location of the longest segment. Segmented hydrophobicity, having in principle a similar "hydrophobic potential" as a contiguous hydrophobicity of equal length, can induce aggregation but, concurrently, alter the modes of assembly into films and micelles.

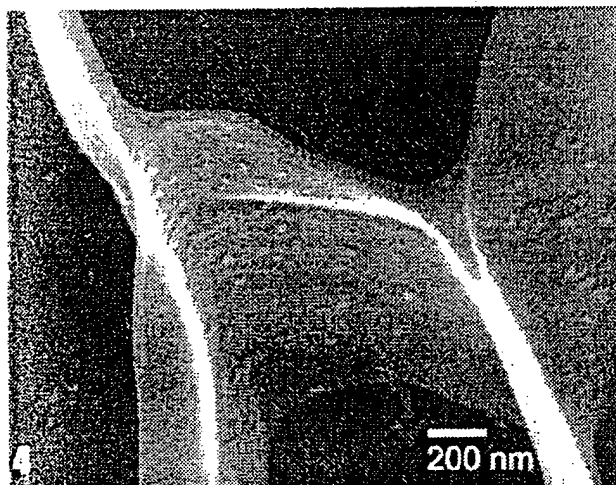
## 2) The Ultrastructure of Frozen Saline Solutions

The instant the temperature drops below 32° F the Armed Forces must confront a serious problem: ice. In the decon area, for example, an aqueous system must be kept above its freezing point if it is to be ready for use at a moment's notice. It was to address this problem that we developed a decon containing an anti-freeze, propylene glycol, and apparently DeconGreen utilizes the same strategy. This led us, quite naturally, to wonder about the fate of water containing simple additives, such as salt and surfactants, when it is frozen. What happens to the salt when saline freezes rapidly? Thus, we used a method, cryo-etch-high resolution scanning electron microscopy or cryo-etch-HRSEM (which Emory is fortunate to possess in our chemistry department), to investigate the freezing of solutions and the fate of the solutes within them.

In a typical experiment, 10  $\mu$ L of a 2-5 wt % aqueous NaCl solution was sandwiched between two gold planchettes. The sample was then loaded into a Balzers HPM 010 high-pressure freezer where liquid nitrogen was sprayed from two sides of a pressurized chamber (2.1 kbar). Freezing the sample from 20 to  $-105^{\circ}$  C took place in 5-6 msec ( $22000-25000^{\circ}$  C/s). After freezing, the sample was immediately immersed in liquid nitrogen to maintain a temperature below  $-170^{\circ}$  C. Next, the sample was placed into a Gatan 3500 CT cryostage precooled to  $-170^{\circ}$  C. A cold blade was then used to fracture the specimen and expose a fresh surface. Etching and coating of this surface were carried out after transferring the cryostage to a Denton DV-602 chromium coater where a vacuum of  $2 \times 10^{-7}$  Torr was maintained. Thus, the temperature was raised from  $-170^{\circ}$  to  $-125^{\circ}$  or  $-105^{\circ}$  C for time periods ranging from 5 to 120 min to allow the exposed ice to vaporized by sublimation ("etching"). Once the etching was completed, the sample was cooled back to  $-170^{\circ}$  C and sputter-coated with chromium at a rate of 0.3 A/s using a current and voltage of 50 mA and 300 V, respectively, under a  $5 \times 10^{-3}$  Torr atmosphere of argon. The resulting 2-nm Cr film has the advantage of possessing smaller grain sizes that do the precious metals. Finally, the sample was removed from the coater and transferred to a DS-130F field emission scanning electron microscope (beam diameter = 1 nm) fitted with dual coldfinger anti-contamination traps and a Varian 860 cold-cathode gauge for monitoring the vacuum at the specimen. Images (4.8 MB) recorded in 16 s at  $-120^{\circ}$  C with a Pentium-based GW video capture board, were processed using Adobe Photoshop 6.0 as TIF files.

The upshot of this rather technical method was that granular icy "fences" were seen surrounding empty areas where amorphous ice had originally resided (see

picture below). The presence of such fences suggests that, during freezing, saline can purge itself of salt with remarkable speed (5-6 msec). Alternatively, channels (perhaps routed around submicroscopic crystallites of cubic ice ( $I_c$ ) embedded in the amorphous ice at  $-105^\circ\text{C}$ ) can guide the migration of salt to the periphery of ice patches. Aside from the fundamental interest of these results, salt morphologies are important to biologists who may encounter fences when examining buffered samples by cryo-etch methods. The results also pertain to the rapid freezing of sea water on cold metal surfaces such as presented by ships and aircraft. In general, the study of frozen solutions merits considerable more attention.



NaCl, 2 wt %, subjected to HPF and etched for 10 min at  $-105^\circ\text{C}$

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE Oct. 29, 2004		3. REPORT TYPE AND DATES COVERED Final Report 01 May 01 - 31 Aug 04	
4. TITLE AND SUBTITLE New Colloidal Systems with Practical Ramifications				5. FUNDING NUMBERS DAAD19-01-1-0551	
6. AUTHOR(S) Fredric M. Menger					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Emory University				8. PERFORMING ORGANIZATION REPORT NUMBER 5-29601	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER 41685.1 - CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  This Final Report begins with a description of two catalysts and one microemulsion that are effective decon systems for mustard and nerve agent simulants. It then describes new ester-modified surfactants synthesized in the hopes that they would provide enhanced solubilization power. In the process, a comparison was made between contiguous and segmented hydrophobicity, the first such comparison of its kind. Surfactants were found to differ in their cmc, foaming, area of occupancy at the air/water interface, and solid-adsorption and solubilization power depending on the location of the ester groups within the chains. Finally, the first cryo-etch-high resolution scanning electron microscopy study of aqueous saline was carried out in order to learn how salt is excluded from frozen water.					
14. SUBJECT TERMS surfactants, micelles, solubilization, ice, electron microscopy,				15. NUMBER OF PAGES 7	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

Enclosure 1